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Improved quantum calculation of the vibrational excitation of H_2 in collinear collisions with helium

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Abstract. The vibrational excitation probabilities of H_2 in collinear collisions with He are calculated quantum mechanically, using the Fredholm integral method. Important differences are found when the accurate H_2 molecular potential of Kołos and Wolniewicz is used instead of the less accurate Morse potential used extensively in previous work. The approximation of truncating the infinite set of coupled equations describing the collision problems is tested, and an alternative closure approximation is suggested to provide an indication of the effect of truncation on the results.

1. Introduction

Several quantum mechanical studies have now been made of the vibrational excitation of diatomic molecules in linear collisions with atoms (Secrest and Johnson 1966, Clark and Dickinson 1973 and earlier references therein). The previous calculations have involved, among others, two important approximations: (i) the approximation of the diatomic molecular potential by either an harmonic oscillator or a Morse potential. Much more accurate wavefunctions for the H_2 molecule exist than are obtained from either the harmonic oscillator or the Morse potential. In particular, the Morse potential does not contain the correct number of bound states. The exact wavefunctions for the accurate potential of Kołos and Wolneiwicz (1965, 1968) can be conveniently represented with a 60-term harmonic oscillator basis set (Lin and Drake 1972), including a discrete representation of the continuum; (ii) the truncation of the infinite set of coupled equations to a finite set. It has been claimed (Clark and Dickinson 1973) that the resulting transition probabilities are exact, provided that convergence is obtained with the number of channels included in the calculation. This may seem reasonable when the molecular spectrum is discrete, as in the harmonic oscillator model, but it is by no means obvious when there is a continuous spectrum.

The aim of the present work is to test the above two approximations for the vibrational excitation of H_2 in collision with He. Throughout, we use the same He–H_2 interaction potential as was used by Clark and Dickinson (1973) to enable a direct comparison to be made with their harmonic oscillator and Morse potential calculations. In addition, we extend the Fredholm integral method (FIM), which has previously been very successful in single channel calculations (Holt and Santoso 1972, 1973), to coupled channel calculations. The results provide an interesting test of the validity of the corresponding semiclassical calculations of Drake and Lin (1974a, b).

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2. Theory

The collision problem has been described in detail elsewhere (eg Rapp and Kassal 1969, Clark and Dickinson 1973).

Following Secrest and Johnson (1966), and Clark and Dickinson (1973), the Schrödinger equation describing the collinear collision of atom A with the diatomic molecule BC may be written as

$$\left[-\frac{1}{2m}\frac{\partial^2}{\partial x^2}-\frac{1}{2}\frac{\partial^2}{\partial y^2}+V_{\mathrm{BC}}(y)+V_{\mathrm{AB}}(x-y)\right]\psi(x,y)=\tfrac{1}{2}E\psi(x,y) \tag{1}$$

where

$$m=\frac{m_{\mathrm{A}}m_{\mathrm{C}}}{m_{\mathrm{B}}(m_{\mathrm{A}}+m_{\mathrm{B}}+m_{\mathrm{C}})} \tag{2}$$

and the interaction between the atom and the molecule is assumed to be a function of the distance AB only.

The eigenfunctions $\{\chi_n(y)\}$ and eigenvalues $\{\epsilon_n\}$ of the diatomic molecule satisfy

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial y^2}+V_{\mathrm{BC}}(y)\right]\chi_n(y)=\epsilon_n\chi_n(y). \tag{3}$$

We shall adopt the formalism of Secrest and Johnson (1966) rather than that of Clark and Dickinson (1973), since the former allows a more satisfactory treatment of closed channels.

We seek a solution of equation (1) satisfying the following boundary conditions, assuming the molecule initially to be in the vibrational state $\chi_I(y)$

$$\lim_{x\to\infty}\psi_I(x,y)=\chi_I(y)\exp(-\mathrm{i}k_Ix)+\sum_{N=0}^{\infty}R_N^I\chi_N(y)\exp(\mathrm{i}k_Nx) \tag{4a}$$

$$\lim_{x\to-\infty}\psi_I(x,y)=\sum_{N=0}^{\infty}T_N^I\chi_N(y)\exp(-\mathrm{i}k_Nx) \tag{4b}$$

where $\{R_N^I\}$, $\{T_N^I\}$ are the reflection and transmission coefficients respectively,

$$T_N^I=0 \text{ for open channels} \tag{5}$$

and $k_N^2=m(E-\epsilon_N)$ for all N.

The probability of finding the oscillator in state $\chi_N(y)$ after the collision is

$$P_{I\to N}=\frac{k_N}{k_I}|R_N^I|^2 \tag{6}$$

where, by conservation of flux,

$$\sum_N P_{I\to N}=1. \tag{7}$$

Following Secrest and Johnson (1966) we may rewrite equation (1) in the integral equation form

$$\psi^I(x,y)=\chi_I(y)\exp(-\mathrm{i}k_Ix)+\sum_M\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{m}{2\mathrm{i}k_M}\chi_M(y)\chi_M(y')\exp(\mathrm{i}k_M|x-x'|)V_{\mathrm{AB}}(x'-y')\psi_I(x',y')\,\mathrm{d}x'\,\mathrm{d}y' \tag{8}$$

and hence examining the asymptotic behaviour as $x \to \pm\infty$ gives

$$R_N^I = \frac{m}{2ik_N}\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \exp(-ik_N x) V_{AB}(x-y)\chi_N(y)\psi_I(x,y) \tag{9}$$

$$T_N^I = \frac{m}{2ik_N}\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \exp(ik_N x) V_{AB}(x-y)\chi_N(y)\psi_I(x,y). \tag{10}$$

We now treat equation (8) by the FIM and assume the separable form taken by previous authors

$$V_{AB}(x-y) = V_0 V_1(x) V_2(y). \tag{11}$$

We premultiply equation (8) by $\exp(-iKx)\chi_J(y)V_{AB}(x-y)$, where K, J are arbitrary, and integrate with respect to both x and y over $(-\infty, +\infty)$. Thus equation (8) becomes

$$\begin{aligned}\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \exp(-iKx)\chi_J(y)V_{AB}(x-y)\psi_I(x,y) \\ = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \exp(-iKx)\chi_J(y)V_{AB}(x-y)\chi_I(y)\exp(-ik_I x) \\ + \sum_M \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \frac{m}{2ik_M}\exp(-iKx)\chi_J(y)V_{AB}(x-y)\chi_M(y) \\ \times \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' \chi_M(y')\exp(ik_M|x-x'|)V_{AB}(x'-y')\psi_I(x',y').\end{aligned} \tag{12}$$

We assume the Fourier expansion

$$\psi_I(x,y) = \sum_S \int_{-\infty}^{\infty} C_S^I(k,k_I)\chi_S(y)\exp(ikx)\,dk \tag{13}$$

and define

$$\langle K|V_1|k\rangle = \int_{-\infty}^{\infty} \exp(-iKx)V_1(x)\exp(ikx)\,dx \tag{14}$$

$$\langle J|V_2|I\rangle = \int_{-\infty}^{\infty} \chi_J(y)V_2(y)\chi_I(y)\,dy \tag{15}$$

$$\langle K|V_1 G_N V_1|k\rangle = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dx' \exp(-iKx)V_1(x)\exp(ik_N|x-x'|)V_1(x')\exp(ikx'). \tag{16}$$

Then applying equations (11) and (13) to (12) gives

$$\begin{aligned}\sum_S \int_{-\infty}^{\infty} dk\, V_0\langle K|V_1|k\rangle\langle J|V_2|S\rangle C_S^I(k,k_I) \\ = V_0\langle K|V_1|-k_I\rangle\langle J|V_2|I\rangle + \frac{mV_0^2}{2i}\sum_M \frac{1}{k_M}\sum_S \int_{-\infty}^{\infty} dk\,\langle J|V_2|M\rangle \\ \times\langle M|V_2|S\rangle\langle K|V_1 G_M V_1|k\rangle C_S^I(k,k_I)\end{aligned} \tag{17}$$

or

$$\sum_S \int_{-\infty}^{\infty} C_S^I(k, k_I)\,\mathrm{d}k \left[\langle K|V_1|k\rangle\langle J|V_2|S\rangle - \frac{mV_0}{2\mathrm{i}} \sum_M \frac{1}{k_M}\langle J|V_2|M\rangle\langle M|V_2|S\rangle\langle K|V_1 G_M V_1|k\rangle \right]$$
$$= \langle K|V_1|-k_I\rangle\langle J|V_2|I\rangle. \tag{18}$$

Similarly we have

$$R_N^I = \sum_S \frac{mV_0}{2\mathrm{i}k_N} \int_{-\infty}^{\infty} \langle k_N|V_1|k\rangle\langle N|V_2|S\rangle C_S^I(k, k_I)\,\mathrm{d}k \tag{19a}$$

and

$$T_N^I = \sum_S \frac{mV_0}{2\mathrm{i}k_N} \int_{-\infty}^{\infty} \langle -k_N|V_1|k\rangle\langle N|V_2|S\rangle C_S^I(k, k_I)\,\mathrm{d}k. \tag{19b}$$

We now approximate the integrals in equations (18) and (19) by a q point quadrature with a set of weights and pivots

$$\{w_\lambda\}, \{k_\lambda\}, \lambda = 1, \ldots, q \tag{20}$$

and write

$$C_S^I(k_\lambda, k_I) = x_\lambda^{(S)}. \tag{21}$$

Equation (18) will no longer hold for arbitrary K, J, but we may choose K to have q arbitrary values, which we choose to be the set $\{k_\lambda\}$. Equations (18) and (19) then reduce to an infinite set of linear equations. Secrest and Johnson (1966) and Clark and Dickinson (1973) truncated their infinite sets of coupled equations by retaining only the terms involving the lowest j states. Clark and Dickinson (1973) argued that if they obtained convergence as j increased, then they had converged to the 'exact' value. This seems reasonable when one is dealing with a discrete spectrum, but it is by no means obvious if the spectrum contains a continuum. As a test of the truncation procedures, we have used two different treatments: Case (i), we follow Secrest and Johnson (1966) and only include terms involving the states for which $S \leqslant j$. This we refer to as *Truncation*. Case (ii), we include the Fourier coefficients $C_S^I(k, k_I)$ for states with $S \leqslant j$, but allow for the remaining states in the sum over all states in equation (18) by using closure. Thus we assume that for $M > j$

$$\frac{1}{k_M}\langle J|V_2|M\rangle\langle M|V_2|S\rangle\langle K|V_1 G_M V_1|k\rangle$$
$$\simeq \frac{1}{k_{j+1}}\langle J|V_2|M\rangle\langle M|V_2|S\rangle\langle K|V_1 G_{j+1} V_1|k\rangle \tag{22}$$

and hence

$$Q_j(J, S) \equiv \sum_{M=1}^{j} \langle J|V_2|M\rangle\langle M|V_2|S\rangle \left[\frac{\langle K|V_1 G_M V_1|k\rangle}{k_M} - \frac{\langle K|V_1 G_{j+1} V_1|k\rangle}{k_{j+1}} \right] + \frac{\langle J|V_2^2|S\rangle\langle K|V_1 G_{j+1} V_1|k\rangle}{k_{j+1}}$$
$$\simeq \sum_M \frac{1}{k_M}\langle J|V_2|M\rangle\langle M|V_2|S\rangle\langle K|V_1 G_M V_1|k\rangle. \tag{23}$$

This case we call *Closure*. In both cases, we have the set of matrix equations

$$\begin{aligned} \boldsymbol{A}\boldsymbol{x} &= \boldsymbol{b} \\ R_N^I &= \boldsymbol{d}^T\boldsymbol{x} \\ T_N^I &= \boldsymbol{e}^T\boldsymbol{x} \end{aligned} \tag{24}$$

where, with $\mu = (\lambda-1)j+M$

$$\begin{aligned} x_\mu &= x_\lambda^{(M)} \\ b_\mu &= \langle k_\lambda|V_1|-k_I\rangle\langle M|V_2|I\rangle \\ d_\mu &= \frac{mV_0}{2ik_N}\langle k_N|V_1|k_\lambda\rangle\langle N|V_2|M\rangle \\ e_\mu &= \frac{mV_0}{2ik_N}\langle -k_N|V_1|k_\lambda\rangle\langle N|V_2|M\rangle. \end{aligned} \tag{25}$$

For case (i)

$$A_{\mu,\mu'} = \langle k_\lambda|V_1|k_{\lambda'}\rangle\langle M|V_2|M'\rangle + \tfrac{1}{2}imV_0\sum_{\tilde{N}=1}^{j}\frac{1}{k_{\tilde{N}}}\langle M|V_2|\tilde{N}\rangle\langle\tilde{N}|V_2|M'\rangle\langle k_\lambda|V_1G_{\tilde{N}}V_1|k_{\lambda'}\rangle \tag{26a}$$

and for case (ii)

$$A_{\mu,\mu'} = \langle k_\lambda|V_1|k_{\lambda'}\rangle\langle M|V_2|M'\rangle + \tfrac{1}{2}imV_0Q_f(M,M'). \tag{26b}$$

For comparison purposes, $V_{AB}(x-y)$ was chosen to coincide with that used by Clark and Dickinson (1973). Hence

$$V_{AB}(x-y) = V_0\exp[-0{\cdot}314(x-y)]. \tag{27a}$$

As pointed out by Secrest and Johnson (1966) the results are independent of V_0. However, since the matrix elements are infinite if x extends to $-\infty$, we modify the potential by setting

$$V_{AB}(x-y) = \infty \qquad \text{for } x < -L. \tag{27b}$$

We have made two choices for $V_{BC}(y)$: (*a*) the harmonic oscillator potential and (*b*) the potential of Kołos and Wolniewicz (1965, 1968). For (*a*) the exact eigenfunctions were used. For (*b*) the eigenfunctions have been obtained as 60-term expansions of harmonic oscillator functions by Lin and Drake (1972). The eigenfunctions obtained using (*b*) provide very accurate representations of the vibrational states of H_2.

The choices of k pivots depended on the channel. For open channels, $\{k_\lambda\}$ were chosen as follows: (i) $\pm k_N$, (ii) pivots corresponding to (usually) 2 point Gaussian integration in various sub-intervals of the range $(-10k_N, 10k_N)$. The procedure taken was to divide the range into several sub-intervals, and sub-divide until convergence was obtained. A typical example of a resulting sub-interval was $(\pm\rho_\lambda k_N, \pm\rho_{\lambda+1}k_N)$ with $\{\rho_\lambda\} = \{0, 0{\cdot}2, 0{\cdot}4, 0{\cdot}6, 0{\cdot}8, 1{\cdot}0, 1{\cdot}2, 2{\cdot}0, 10{\cdot}0\}$. The $\{\rho_\lambda\}$ were not necessarily the same for each N. For the closed channels the $\{k_\lambda\}$ corresponded to Gaussian integration in various sub-intervals of $(-4{\cdot}0, +4{\cdot}0)$. With this choice of pivots three important points should be noted:

(i) The equations may be arranged so that the (complex) matrix $\boldsymbol{A}$ is symmetric, thereby saving storage:
(ii) $\boldsymbol{A}$ is the same for all initial channels.
(iii) Detailed balancing is satisfied.

The calculation of the first and second Born terms involved in equation (18) is very straightforward, the following integrals being required:

$$\int_{-L}^{\infty} \exp\{-[\alpha+\mathrm{i}(K-k)]x\}\,\mathrm{d}x = \frac{\exp[\alpha+\mathrm{i}(K-k)]L}{\alpha+\mathrm{i}(K-k)} \tag{28}$$

$$\int_{-L}^{\infty}\mathrm{d}x\int_{-L}^{\infty}\mathrm{d}x'\exp[-(\alpha+\mathrm{i}K)x+\mathrm{i}k_N|x-x'|-(\alpha-\mathrm{i}k)x']$$

$$=\frac{\exp[2\alpha+\mathrm{i}(K-k)]L}{2\alpha+\mathrm{i}(K-k)}\left[\frac{1}{\alpha-\mathrm{i}(k+k_N)}+\frac{1}{\alpha+\mathrm{i}(K-k_N)}\right].$$

The matrix elements $\langle N|V_2|M\rangle$ may be constructed from those for the harmonic oscillator, which are given by Clark and Dickinson (1973).

3. Results and discussion

For the harmonic oscillator model we have performed calculations for E = 4, 6, 8, 10, 12 ($\frac{1}{2}\hbar\omega_e$) normally including one closed channel in each calculation (see table 1). Calculations have been performed for both cases detailed in equation (26). There is no significant difference between the results, indicating that truncation is a valid procedure for this model. Our results agree with those given by Clark and Dickinson to within their approximate 1% error.

For the Kołos and Wolniewicz model we have performed calculations also for E = 4, 6, 8, 10, 12 ($\frac{1}{2}\hbar\omega_e$), using $\omega_e = 4400\,\mathrm{cm}^{-1}$ (Herzberg and Howe 1959). Only for the lowest energy is one closed channel sufficient. At higher energies we have found that at least three closed channels must be included in the calculation to obtain good agreement between the values with and without closure as shown by the results in table 2. The values obtained from this model may be compared (see table 3) with our harmonic oscillator values and the Morse oscillator values given by Clark and Dickinson (1973). The large differences between the harmonic and Morse oscillator values have already been noted by Clark and Dickinson. No less significant, though not as pronounced, is the fact that the inelastic transition probabilities we have obtained using the Kołos and Wolniewicz potential lie about 25% lower than the Morse results for all the energies in table 3. Two points are clear: (i) the transition probabilities are sensitive to the molecular potential assumed; (ii) it is much more important to consider the influence of the closed channel states for an anharmonic potential. The reason for this seems to be that whereas the matrix elements $\langle N|V_2|M\rangle$ are all positive for the harmonic oscillator, for the Morse and for the Kołos and Wolniewicz potential some are negative. In consequence, the terms which *Closure* includes, but *Truncation* excludes, which are approximately proportional to

$$\sum_{N>j}\langle J|V_2|N\rangle\langle N|V_2|M\rangle$$

may not be insignificant for many of the j channels included in the calculation. Hence the test of using closure seems to be a useful one. It does not *guarantee* convergence to the correct result, but at least it provides some indication of the effect of truncation. It is, of course, possible that for other models of the atom–molecule interaction the harmonic oscillator model may not have all its matrix elements positive, and that a larger number of closed channels would need to be retained. The results show that the truncation

Table 1. Harmonic oscillator transition probabilities with and without closure.

Transition	No closure	Closure	Clark and Dickinson (1973)
$E = 4$			
0–1	7·22(−4)	7·22(−4)	7·20(−4)
$E = 6$			
0–1	2·95(−2)	2·95(−2)	2·95(−2)
0–2	1·07(−5)	1·08(−5)	1·07(−5)
1–2	1·43(−3)	1·43(−3)	1·42(−3)
$E = 8$			
0–1	1·32(−1)	1·32(−1)	1·33(−1)
0–2	2·02(−3)	2·03(−3)	2·04(−3)
0–3	5·25(−7)	4·74(−7)	4·96(−7)
1–2	5·50(−2)	5·51(−2)	5·50(−2)
1–3	3·07(−5)	3·10(−5)	3·07(−5)
2–3	2·11(−3)	2·12(−3)	2·10(−3)
$E = 10$			
0–1	2·90(−1)	2·90(−1)	2·92(−1)
0–2	2·22(−2)	2·22(−2)	2·25(−2)
1–2	2·16(−1)	2·16(−1)	2·17(−1)
1–3	5·36(−3)	5·36(−3)	5·39(−3)
2–3	7·69(−2)	7·70(−2)	7·70(−2)
2–4	2·77(−3)	2·77(−3)	2·76(−3)
$E = 12$			
0–1	4·26(−1)	4·25(−1)	4·28(−1)
0–2	8·98(−2)	8·95(−2)	9·13(−2)
1–2	3·68(−1)	3·69(−1)	3·69(−1)
1–3	5·17(−2)	5·20(−2)	5·24(−2)
2–3	2·67(−1)	2·69(−1)	2·68(−1)
2–4	9·46(−3)	9·56(−3)	9·55(−3)
3–4	9·57(−2)	9·52(−2)	9·59(−2)
3–5	9·25(−5)	9·29(−5)	9·28(−5)
4–5	3·42(−3)	3·44(−3)	3·40(−3)

Table 2. Transition probabilities for the Kolos and Wolniewicz potential showing the convergence with the number of closed channels with and without closure at $E = 8$.

Transition	No closure Number of closed channels			Closure Number of closed channels		
	1	2	3	1	2	3
0–1	2·32(−2)	2·34(−2)	2·35(−2)	2·42(−2)	2·36(−2)	2·35(−2)
0–2	1·07(−4)	1·10(−4)	1·11(−4)	1·22(−4)	1·13(−4)	1·12(−4)
0–3	5·66(−8)	8·11(−8)	5·85(−8)	9·43(−9)	6·68(−8)	5·68(−8)
1–2	1·80(−2)	1·84(−2)	1·85(−2)	1·94(−2)	1·87(−2)	1·86(−2)
1–3	2·00(−5)	2·18(−5)	2·16(−5)	2·41(−5)	2·22(−5)	2·19(−5)
2–3	4·27(−3)	4·64(−3)	4·59(−3)	4·75(−3)	4·70(−3)	4·62(−3)
2–4	2·34(−9)	2·59(−9)	2·63(−9)	3·04(−9)	2·62(−9)	2·65(−9)
3–4	2·12(−6)	2·28(−6)	2·28(−6)	2·30(−6)	2·30(−6)	2·29(−6)

procedure used in most calculations of this type is valid, at least in the range of energies considered.

On the whole the FIM have proved successful in treating this problem. Its advantages are that *Closure* can be used, that the matrix equation can be used for dealing with all possible initial channels simultaneously, and that detailed balancing is satisfied. The value of L (equation 27*b*) was chosen to be 16 au—large enough such that the transition probabilities are not sensitive to variations in L. For the significant transition probabilities $T_N^I \sim 10^{-5} R_n^I$ or smaller, and equation (7) was effectively satisfied. The main disadvantage is that a large number of pivots are required—around 42 for open channels and 24 for closed channels—so that within the size of the machine being used—IBM 360/65—we could only include 9 channels.

We do not quote results for the Kolos and Wolniewicz potential for $E = 12$, because there are 7 open channels and there are significant differences between the *Truncation* and *Closure* results with only two closed channels included.

Comparison of the results of table 3 with the revised semi-classical results of Drake and Lin (1974b) shows that the time-dependent semi-classical approximation seriously overestimates the smaller transition probabilities by an order of magnitude or more. This is at least partly due to the lack of energy conservation. Much better results are obtainable with the extended WKB methods developed by Miller (1970) and Marcus (1971), (see Eastes and Doll 1974 for recent work).

The inclusion of rotationally inelastic effects in a complete three-dimensional calculation has recently been discussed for the Morse potential model of the H_2 molecule (Kouri and Wells 1974, Alexander and Berard 1974). Although Schaefer *et al* (1974) find good agreement for low-energy transitions to the low-lying vibrational states, significant changes can be expected for transitions to the higher vibrational states when the exact H_2 potential is used.

Table 3. Transition probabilities for the Kołos and Wolniewicz potential.

Transition	Energy ($\frac{1}{2}\hbar\omega_e$)†		
	4	6	10
0–1	1·91(−4)	5·59(−3)	5·41(−2)
0–2		1·46(−6)	9·53(−4)
0–3			5·59(−6)
1–2		1·05(−3)	6·57(−2)
1–3			8·31(−4)
1–4			2·15(−6)
2–3			4·72(−2)
2–4			2·12(−4)
3–4			1·72(−2)
3–5			3·33(−6)
4–5			7·61(−4)

† See table 2 for $E = 8$.

References

Alexander M H and Berard E V 1974 *J. Chem. Phys.* **60** 3950–7
Clark A P and Dickinson A S 1973 *J. Phys.* B: *Atom. Molec. Phys.* **6** 164–80
Drake G W F and Lin C S 1974a *J. Phys.* B: *Atom. Molec. Phys.* **7** 398–405
—— 1974b *J. Phys.* B: *Atom. Molec. Phys.* **7** 2440
Eastes W and Doll J D 1974 *J. Chem. Phys.* **60** 297–302
Herzberg G and Howe L L 1959 *Can. J. Phys.* **37** 636–59
Holt A R and Santoso B 1972 *J. Phys.* B: *Atom. Molec. Phys.* **5** 497–507
—— 1973 *J. Phys.* B: *Atom. Molec. Phys.* **6** 2010–7
Kołos W and Wolniewicz L 1965 *J. Chem. Phys.* **43** 2429–41
—— 1968 *J. Chem. Phys.* **49** 404–10
Kouri D J and Wells C A 1974 *J. Chem. Phys.* **60** 2296–304
Lin C S and Drake G W F 1972 *Chem. Phys. Lett.* **16** 35–7
Marcus R A 1971 *J. Chem. Phys.* **54** 3965–79
Miller W H 1970 *J. Chem. Phys.* **53** 1949–59
Rapp D and Kassal T 1969 *Chem. Rev.* **69** 61–102
Secrest D and Johnson B R 1966 *J. Chem. Phys.* **45** 4556–70
Schaefer, J, Lester W A Jr, Kouri D and Wells C A 1974 *Chem. Phys. Lett.* **24** 185